1s CORE-LEVEL SHIFTS IN Al CLUSTERS OF INCREASING SIZE

by

I.Gyémánt* and Zs.Varga

Department of Theoretical Physics, József Attila University, P.O.B. 105, H-6701 Szeged, Hungary

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The Al 1s core-electron binding energy shifts have been calculated for Al_{13} and Al_{19} clusters by the MS Xα method. The atom/cluster shifts calculated as the differences between the Slater transition-state energies for the 1s levels are 5.50 eV and 2.68 eV, for Al_{13} and Al_{19}, respectively. These values are to be compared with the corresponding calculated Xα ΔSCF results of 5.27 eV and 2.75 eV .

The determination of core-electron binding energy shifts has been attracting great interest and the significance of this problem is shown by the large number of papers published on this subject recently. The considerable amount of experimental and theoretical work has been motivated by the success of the use of soft X-rays (e.g. the Al Kα line with an energy of 1487 eV and the Mg Kα line with energy of 1254 eV) to study core levels with high resolution ($\sim$0.1 eV) [1-2]. It was early realized that the core-level energies depend on the chemical environment of the atom and are systematically several eV lower in conducting solids than in free atoms [3]. Measurements and calculations on the atom/molecule binding energy shifts have been performed for O_3, S_8, P_4, As_4 and Se_n [4-5]. It has been recognized that binding energy shifts reflect not only the ground-state charge distribution of the molecule, but also the energy associated with the rearrangement of the passive electrons in the final state. Results for F/F_2, Cl/Cl_2, Br/Br_2 and Na/Na_3 [6-7] show that without final-state effects the 1s binding energies would be higher in the molecule than in the atom, so that ΔSCF calculations, i.e. SCF calculations both for the initial and for the final state, have to be done.

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The core-level binding energy is defined as:

$$E_c = E_f(n_c-1)-E_i(n_c)$$

where $E_i(n_c)$ is the total energy in the initial state with n_c electrons, $E_f(n_c-1)$ is that in the final state with n_c-1 electrons, and n_c is the initial occupancy of the core level c. Nevertheless, in the Xα approximation [8] the core-level binding energy can be approximated well by the Slater transition-state energy.

In this paper we present ΔSCF and transition-state results calculated with the MS Xα method for Al 1s core-level atom/cluster shifts in clusters of 13 and of 19 Al atoms. The method was suggested by Slater [8] and was applied to calculate molecular ESCA spectra by Connolly et al. [9]. The geometry of the Al_{13} cluster corresponds to an Al atom and its 12 nearest neighbours in bulk Al of fcc structure with the lattice constant 404.3 pm. For Al_{19} the 2nd shell of 6 nearest neighbours has been included as well.

The muffin-tin version of the MS Xα cluster MO method has been used [10]. The atomic region consists of atomic spheres 142.9 pm in radius around each of the atomic nuclei. The atomic spheres are enclosed in a sphere 428.8 pm in radius, the outer sphere, centred at the central atomic nucleus.The potential is spherically averaged inside the atomic spheres, as well as outside the outer sphere, and it is taken to be constant in the interatomic region, the region inside the outer sphere and outside the atomic spheres. The exchange parameter, α , has been chosen to be 0.7285 [11].

The 1s core-level binding energy for a free Al atom has been determined as the corresponding transition-state energy, which turned out to be -1577.23 eV, and we have used this value when calculating binding energy shifts. In Al clusters, the 1s level of the central Al atom has been studied, so that the symmetry of the cluster need not be changed on ionization, i.e. the O_h symmetry group could be used both in the initial and in the final states.

For Al_{13} the transition-state energy of the 1s level is -1571.73 eV and the difference in the total energies after and before the ionization gives 1571.96 eV. The corresponding values for an Al_{19} cluster are -1574.55 and 1574.48 eV, respectively.

The free-atom/cluster shift in a SCF calculation is given by the difference:

$$\Delta = E_{c,atom} - E_{c,cluster}$$

which can be approximated as the difference in the transition-state energies:

$$\delta = |\varepsilon_{c,atom}| - |\varepsilon_{c,cluster}| .$$

For the Al_{13} cluster, δ =5.5 eV and Δ =5.27 eV have been obtained, i.e. transition-state energies can be used only to estimate total energy differences, considering that binding energies can be measured to an accuracy of 0.1 eV or better with XPS. Though no experimental and no theoretical results have been reported for Al clusters, both experimental and theoretical data are available for atom/metallic aluminium 1s core-level shifts. Experimental values for solid-state shifts are obtained either from direct simultaneous vapour-solid measurements or from comparison between calculated or measured atomic energies and separate solid-state measurements. The 1s binding energy 1568.8 eV of a free Al atom has been obtained semiempirically by Aksela et al. [12] in the following way.

The relativistic relaxed-orbital binding energy value 1567.87 eV of Huang et al.[13] was used as the starting value. The experimental free-atom binding energy value of 1568.4 eV was obtained from the thermochemical model [14] combined with X-ray data [15-16]. Because the deviations of the experimental free-atom binding energies from the *ab initio* calculations are systematic and slowly varying linear functions of Z in the series Ne, Na, Mg, Al, Si, P, S, Cl and Ar, Aksela et al. used linear interpolation for the correction by selecting the data on Ne and Ar as reference values.

An experimental solid-state 1s binding energy of 1558.2 eV relative to the Fermi level has been determined by Castle et al. [17] . This value has to be corrected by the work function of 4.28 eV [18] in order to obtain the binding energy relative to vacuum.

In this way, the experimental value of the atom/metal 1s binding energy shift for Al is 6.3 eV [12] .

Various theoretical models, such as the "excited-atom approach" [19] , the thermochemical model [20] ,etc., have been proposed. Spin-polarized density-functional conduction-electron screening calculations have been performed for core ionization by Nieminen and Puska [21] and Rantala [22]. The local-density exchange and correlation potential approximation of Gunnarsson and Lundquist [23] has been used in these self-consistent calculations, and for the "atom in jellium vacancy" model 6.3 eV [21] and 6.15 eV [22] have been obtained for the Al atom/solid 1s core-level binding energy shift, in good agreement with the experimental value.

Mali and Kanhere [24] presented results for the "atom in jellium vacancy" model with the exchange and correlation potential of Vashishta and Singwi [25], and they used transition-state theory instead of ΔSCF. However, their result for the 1s level turned out to be rather disappointing, 1.64 eV, too low compared with the experimental value of 6.3 eV. This large deviation is due to the inadequacy of the transition--state concept when the total energy-dependence on occupation number is different from that with an $X\alpha$ type exchange potential.

Taking into account the approximations used in the MS $X\alpha$ calculation, both the ΔSCF result of 5.27 eV and the transition-state result of 5.5 eV can be considered as good estimates and are in good agreement with the expected atom to solid trend of the binding energies.

However, the corresponding values for the Al_{19} cluster are 2.75 eV and 2.68 eV, respectively. These values are rather disappointing, since values higher than 5.27 eV would have been expected. This unexpected deviation is due to the artificial construction of the muffin-tin potential.The interatomic

region increases with increasing cluster size, and the proportions of the interatomic regions to the regions inside the atomic spheres are 0.519, 0.661 and 0.517 for Al_{13}, Al_{19} and Al_{43}, respectively. Therefore, the muffin-tin potentials are badly off in the case of Al_{19} and are expected to be realistic for Al_{13} and Al_{43}. Calculations for Al_{43} are now in progress, and results will be presented in a forthcoming paper.

REFERENCES

[1] Siegbahn,K., C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.-E. Karlsson, I. Lindgren, B. Lindberg: ESCA-Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy, North-Holland, 1967.

[2] Siegbahn,K. C. Nordling, G. Johansson, J. Hedman, P. F. Hedén, K. Hamrin, U. Gelius, T. Bergmark, L.O. Werme, R. Manne, Y. Baer: ESCA Applied to Free Molecules, North Holland, 1969.

[3] Shirley,D.A., R. L. Martin, S. P. Kowalczyk, F. R. McFeely, L. Ley: Phys. Rev. B15 544 (1977)

[4] Banna,M.S.: Contemp. Phys. 25, 159. (1984)

[5] Beck,D.R., R. J. Key, A. R. Slaughter, R. D. Mathews, M. S. Banna: Phys. Rev. A28, 2643 (1983)

[6] Martin,R.L., E.R. Davidson: Phys. Rev. A16,1341(1977)

[7] Martin,R.L., D. A. Shirley: Electron Spectroscopy: Theory, Techniques and Applications. Vol. 1. Ed. by C. R. Brundle, A.D. Baker,Academic Press,1978. pp.76-117.

[8] Slater,J.C.: The Self-Consistent Field for Molecules and Solids, Vol.4, McGraw-Hill, New York, 1974.

[9] Connolly,J.W.D., H. Siegbahn, U. Gelius, C. Nordling: J. Chem. Phys. 58, 4265 (1973)

[10] Liberman,D., J. R. Batra: Multiple Scattering Program Description. IBM Thomas J. Watson Research Center, New York, 1973.

[11] Schwarz,K.: Phys. Rev. B5, 2466 (1972)

[12] Aksela,S., R. Kumpula, H. Aksela, J. Väyrynen: Phys. Scripta 25, 45 (1982)

[13] Huang,K.N., M.Ayoagi, M.Chen, B. Crasemann, H.Mark: Atomic Data and Nuclear Data Tables 18, 243 (1976)

[14] Johansson,B., N. Mårtensson: Phys.Rev. B21,4427(1980)
[15] Moore,C.E.: Atomic Energy Levels Circ. 467, Washington: Nat. Bur.stand (1971)
[16] Bearden,J.A., Rev. Mod. Phys. 39, 78 (1967)
[17] Castle,J.E., L. B. Hazell, R. D. Whitehead: J. Electron Spectrosc. 9, 247 (1975)
[18] CRC Handbook of Chemistry and Physics, 58th Edition, CRC Press, Cleveland, 1977.
[19] Watson,R.E., M.L.Perlman, J.F.Herbst: Phys. Rev. B13, 2358 (1976)
[20] Steiner,P., S.Hüfner, N.Mårtensson, B.Johansson: Solid State Commun. 37, 73 (1981)
[21] Nieminen,R.M., M.J. Puska: Phys. Rev. B25, 67 (1982)
[22] Rantala,T.T.: Phys. Rev. B28, 3182, (1983)
[23] Gunnarsson,O., B.I.Lundquist:Phys.Rev. B13,4274 (1976)
[24] Mali,S.J.,D.G.Kanhere:phys.stat.sol.(b)125,K143 (1984)
[25] Vashishta,P., K.S.Singwi: Phys. Rev. B6, 875, (1972)

СДВИГИ 1s УРОВНЯ В КЛАСТЕРАХ АЛЮМИНИЯ С УВЕЛИЧЕНИЕМ ИХ РАЗМЕРОВ

И.Н. Дьемант, Ж. Варга

Вычислены сдвиги энергии связи 1s электрона алюминия в кластерах алюминия Al_{13} и Al_{19} методом многократного рассеяния в Хα приближения самосогласованного поля.Сдвиги 1s уровня, вычисленные разностями энергий переходных состояний, были 5.50 эВ в кластере Al_{13} и 2.68 эВ в Al_{19}. Эти величины сравнимы со сдвигами 5.27 эВ и 2.75 эВ вычисленными из разностей Хα полной энергии.